Phase Diagrams for Ternary Liquid Systems

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Needing an undergraduate experiment on three-component systems for students of engineering, we turned to the paper by J. R. Clarke.1 He advocated the use of the ternary liquid system 1,2-dichloroethane (DCE) + ethanoic acid + water and showed how the binodal curve and tie lines could be obtained by students in a normal three-hour practical session. However, his method required the provision of calibration curves of refractive indices for the analysis of the mixtures at the ends of the tie lines.

When planning to use this experiment it became obvious that a very simple adaptation of the original Clarke procedure would allow the experiment to stand alone without the calibration curves.

In the first part of the experiment the position of the binodal curve is determined. Starting with a known initial mixture of the immiscible pair of liquids water + DCE, ethanoic acid is added from a buret until a homogeneous solution is obtained. The innovation is simply to sample this homogeneous liquid and measure its refractive index. Not only has a point on the binodal curve been fixed, but its refractive index is also known. From a series of such measurements the binodal curve can be drawn, and refractive indices can be added to the curve. Actual values vary smoothly from 1.3330 for water to 1.4443 for DCE.

In the second part of the experiment, ternary mixtures of the liquids are made up and shaken in separating funnels. The upper and lower layers are sampled, and refractive indices determined. The overall composition can be calculated from the volumes used, and the compositions of the two phases can be determined by linear interpolation between known points on the binodal curve. A straight line should join the two endpoints on the binodal curve and the overall composition.

A mixture of DCE + water was shaken and then sampled; the two refractive indices showed the very limited solubility mentioned by Clarke.1 It would seem that no real inaccuracy is introduced if the mutual solubility is ignored and refractive indices of pure components are used for the endpoints of the binodal curve (also assumed to end at the base apices of the triangle).

The initial mixtures for the binodal curve determination and the tie-line determinations together with typical experimental results are given in Tables 1 and 2 and in the figure.

So long as the Abbe refractometer is calibrated with either water or DCE and the student keeps to one instrument, the actual values obtained are self-consistent but may vary slightly, with no detrimental effect, from the literature values.

The experiment has become free-standing and much more satisfactory for the student; there is a real sense of achievement when the three points fit a straight line.

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